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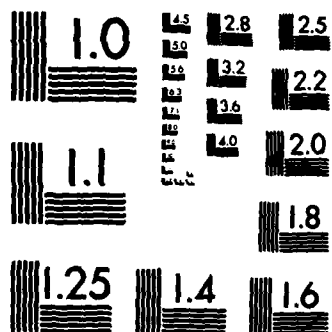
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<p>The techniques of laser double resonance or near-infrared fluorescence detection in combination with direct excitation of overtone vibrations provide detailed data on the rates and pathways of collisional energy transfer in hydrogen fluoride and deuterium fluoride. These measurements yield the self-relaxation rate constants for HF(v=1,2,3,4,5) and DF(v=1,2). In addition, they determine the relative importance of the vibration-vibration and vibration-translation, rotation energy transfer pathways for v<sub>2</sub> in both molecules.</p>		

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Applying these techniques at higher temperatures gives the self-relaxation rate constants between 300 and 700 K for HF( $v=1-5$ ). Using different partners permits the determination of the rate constants for collisional relaxation of HF( $v=3,4,5$ ) by  $H_2$ ,  $D_2$ ,  $CH_4$ ,  $CD_4$ , and  $CO_2$ .

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**FINAL REPORT**

**VIBRATIONAL RELAXATION RATES AND PATHWAYS IN HIGHLY  
EXCITED MOLECULES**

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**INTRODUCTION**

The goal of this project is to use laser double resonance and near-infrared fluorescence techniques in uncovering the detailed pathways of vibrational relaxation in highly vibrationally excited diatomic molecules. Collisional energy transfer is an important process that has significant consequences in a variety of technologically and fundamentally important situations. One example is in chemical lasers, where the shuttling of energy between molecules controls the populations of the vibrationally and rotationally excited states that participate in the laser transitions. Theoretical descriptions of collisional energy transfer incorporate models of interaction potentials and the dynamics of inelastic scattering, and detailed experimental studies are a means of testing the quality of these descriptions.

Our experiments use a very selective energy deposition scheme, laser excitation of an overtone vibration, in combination with time resolved spectroscopic monitoring of the vibrationally excited molecule or its collision partner to determine the energy

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transfer rates and pathways in highly vibrationally excited hydrogen fluoride and deuterium fluoride. Direct excitation of an overtone vibration is a very inefficient but highly specific technique that prepares molecules in single vibrational-rotational states. Thus, we are able to monitor the relaxation of hydrogen fluoride in its first through fifth excited vibrational states ( $v=1$  to  $v=5$ ) by ground state HF and by several other collision partners. We have also extended these experiments to include self-relaxation of deuterium fluoride in  $v=1$  and 2.

The two spectroscopic techniques used in these studies are near-infrared fluorescence and laser double resonance. In the former, we monitor the spontaneous overtone emission from the vibrationally excited molecule with a near-infrared sensitive photomultiplier. In the latter, we monitor the transient gain or absorption of the light from an infrared probe laser as the initially excited molecules relax collisionally. Because the laser double resonance technique probes the collision partner during self-relaxation, it is the means by which we determine the relative importance of the vibration-to-vibration (V-V) and vibration-to-translation, rotation (V-T,R) energy transfer routes in hydrogen fluoride and deuterium fluoride. The most important results of this study are the rate constants for collisional relaxation of HF( $v=1,2,3,4$ , and 5) and DF( $v=1$  and 2) and the relative importance of the competing relaxation pathways for excited vibrational states above  $v=1$  in these molecules.

COLLISIONAL ENERGY TRANSFER IN HF( $v=1,2,3,4$ , and 5)

## Self-relaxation

The vibrational overtone induced near-infrared fluorescence experiments provide the total relaxation rate constants for HF( $v=3,4,5$ )<sup>1</sup> but do give the relative importance of the V-V and V-T,R pathways. Only the more detailed laser double resonance measurements yield these data.<sup>2,3</sup> Because the laser double resonance scheme is particularly well suited to determining the temperature dependences of these quantities, we were also able to extract the rate constants for HF( $v=1$  and 2) and the relative size of the V-V pathway for HF( $v=2$ ) between 300 and 700 K.<sup>3</sup> These results and our earlier near-infrared fluorescence measurements on HF( $v=3,4,5$ ) form a complete set of temperature dependent rate constants over this rather large temperature range. The observed decrease of the rate constants with increasing temperature is characteristic of systems in which long range forces play a central role, and we conclude that a decrease in collision duration is responsible for the smaller rate constants at higher temperatures. We find that the rate constant for self-relaxation of HF( $v=2$ ) declines more slowly than that for  $v=1$ , where only V-T,R transfer is possible, and more slowly than that for  $v \geq 3$ , where V-T,R processes dominate the relaxation. We infer that the V-V relaxation pathway has an inherently weaker dependence on temperature that is reflected in the behavior of HF( $v=2$ ), for which the V-V pathway is the major relaxation route.

Table I summarizes the rate constants and V-V branching fractions for HF( $v=1,2,3,4,5$ ) that we have determined in our

laboratory. The relaxation probability, which is the ratio of the measured energy transfer rate constant to the gas kinetic collision rate constant, is given as a measure of the efficiency of the relaxation process. The rate constants for HF( $v=3,4,5$ ) come from the near-infrared measurements<sup>1</sup> while the rate constants for HF( $v=1$  and 2) and all the branching fractions come from the double resonance experiments.<sup>2-4</sup>

Table I. Experimental rate constants and energy transfer mechanisms for HF( $v=1-5$ ) self-relaxation at room temperature.

Level	Rate Constant <sup>a</sup>	Probability	V-V Branching Fraction
1	0.045±0.003	0.0089	
2	0.61 ±0.03	0.12	0.59±0.10
3	0.98 ±0.10	0.19	0.44±0.05
4	2.36 ±0.09	0.47	0.16±0.05
5	4.89 ±0.26	0.96	~0

(a) Units of  $\mu\text{s}^{-1}\text{Torr}^{-1}$ .

#### Other Collision Partners

Our near-infrared fluorescence measurement have provided some of the most detailed data on total vibrational relaxation rate constants for HF( $v=3,4,5$ ) with a number of stable collision partners.<sup>5</sup> The results for H<sub>2</sub>, D<sub>2</sub>, CH<sub>4</sub>, CD<sub>4</sub>, and CO<sub>2</sub> show systematic trends with the magnitude of the energy defect for V-V energy transfer that reveal it to be the controlling aspect of the



relaxation dynamics. The effect of isotopic substitution is particularly revealing in this regard since it substantially alters the energy defect and rotational constant without changing the intermolecular potential. The variation in the rate constant with vibrational quantum number is quite sharp and shows that simple descriptions based on perturbation theory are unable to describe the dynamics.

One of the most interesting collision partners that we have investigated using the double resonance technique is the relatively unstable hydrogen fluoride dimer.<sup>6</sup> By working at relatively high concentrations, where dimers constitute less than one percent of the total pressure, and deconvoluting the non-linear variation of the observed decay constant with pressure, we are able to extract the relaxation rate constant for HF( $v=1$ ) by the HF dimer. The process is quite efficient and occurs on roughly every other gas kinetic collision. The energy transfer proceeds by a sequential two step pathway in which very efficient, nearly resonant V-V transfer from the monomer produces a vibrationally excited dimer that rapidly predissociates. Using a vibrational predissociation lifetime that is consistent with independent linewidth measurements in this model, we are able to reproduce our observed pressure dependences. A further confirmation of this model comes from new data on relaxation of HF( $v=1$ ) by the DF dimer, which lacks the near resonant V-V pathway. In this case, the energy transfer is too slow to measure, in agreement with our model.

COLLISIONAL ENERGY TRANSFER IN DF( $v=1$  and 2)

The most recent extension of our energy transfer measurements on very polar molecules is a laser double resonance study of the vibrational relaxation rate constants and pathways for self-relaxation of deuterium fluoride in  $v=1$  and  $v=2$ .<sup>7</sup> The rate constant for DF( $v=1$ ) is almost a factor of four smaller than that for HF( $v=1$ ). This result is consistent with a model of the relaxation in which the energy released in V-T,R relaxation preferentially becomes rotation of the initially excited molecule. The smaller rotational constant of DF requires that the change in angular momentum be considerably larger for the same change in rotational energy. This makes self-relaxation of DF( $v=1$ ) slower than that for HF( $v=1$ ). The rate constants for  $v=2$  are more nearly the same because the V-V channel, which is operative in both systems, is less endothermic for DF than HF. In fact, we find that DF( $v=2$ ) relaxes solely by the V-V pathway. Table II summarizes the results of these double resonance measurements on deuterium fluoride. Finally, the decay constant for DF relaxation at higher pressures shows the same non-linear pressure dependence that we observed for HF. This again agrees with the model of rapid sequential relaxation being initiated by V-V energy transfer from the monomer to the dimer.

Table II. Experimental rate constants and energy transfer mechanisms for DF( $v=1$  and 2) self-relaxation at room temperature.

Level	Rate Constant <sup>a</sup>	Probability	V-V Branching Fraction
1	0.012 $\pm$ 0.002	0.0024	
2	0.72 $\pm$ 0.07	0.15	1

(a) Units of  $\mu\text{s}^{-1}\text{Torr}^{-1}$ .

#### REFERENCES

1. Vibrational Relaxation of HF( $v=3,4,5$ ). G. M. Jursich and F. F. Crim, J. Chem. Phys. 74, 4455 (1981).
2. Laser Double Resonance Measurements of Vibrational Energy Transfer Rates and Mechanisms in HF( $v=2$ ). R. A. Copeland, D. J. Pearson, Jeanne M. Robinson, and F. F. Crim, J. Chem. Phys. 77, 3974 (1982).
3. Rates and Pathways of Vibrational Self-relaxation of HF( $v=2$ ) between 300 and 700 K. J. M. Robinson, D. J. Pearson, R. A. Copeland, and F. F. Crim, J. Chem. Phys. 82, 780 (1985).
4. A Direct Determination of the Role of Vibration-to-Vibration Energy Transfer in HF( $v=3,4$ ) Self-relaxation. J. M. Robinson, K. J. Rensberger, and F. F. Crim, J. Chem. Phys. 84, (1986) (in press).
5. Vibrational Relaxation of HF( $v=3,4,5$ ) by H<sub>2</sub>, D<sub>2</sub>, CH<sub>4</sub>, CD<sub>4</sub>, and CO<sub>2</sub>. G. M. Jursich, D. R. Ritter, and F. F. Crim, J. Chem. Phys. 80, 4097 (1984).
6. Collisional Energy Transfer via Vibrational Predissociation: Relaxation of HF( $v=1$ ) by HF Dimers. K. J. Rensberger, R. A. Copeland, J. M. Robinson, and F. F. Crim, J. Chem. Phys. 83, 1132 (1985).
7. Vibrational Relaxation Rates and Pathways for DF( $v=1$  and 2) Self-Relaxation. J.M. Robinson, K.J. Rensberger, M.A. Muyskens, and F.F. Crim, J. Chem. Phys. (to be published); J.M. Robinson, Ph.D. Thesis, University of Wisconsin, 1985.

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